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Nuclear Magnetic Resonance Shift Reagents: Evidence for Different Mechanisms of Contact Contributions to ^{13}C Shifts Induced by Nickel and Cobalt Acetylacetonates with Saturated Amines and Alcohols

(complexes/spin polarization/α-carbon shifts/β-carbon shifts)

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ABSTRACT **The pattern of ^{13}C and ^{1}H nuclear magnetic resonance (NMR) shift changes produced by complexation of cobalt and nickel acetylacetonates with amines and alcohols indicates that there is more than one mode of operation of the contact interaction. A large effect with alternating signs is important at the α and β carbons, but this effect seems to be overlaid by another influence that appears to fall off monotonically as one proceeds away from the site of complexation.**

It is clear that there are large contact contributions to the changes of ^{13}C chemical shifts resulting from complexation of nickel and cobalt acetylacetonates with amines (1–3). With saturated amines, these appear to operate by way of the σ-bond electrons (1–3) and show a propensity for alternation in sign as one proceeds away from the α carbon. Such alternation of sign is usually ascribed to the "spin polarization" mechanism of contact interaction.

In more extended studies of the ^{13}C shifts of amines induced by $Co(AcAc)_2$ and $Ni(AcAc)_2$ of saturated amines and alcohols (Table 1), a picture emerges that seems substantially more complex. In the first place, with $Ni(AcAc)_2$, the α shifts are invariably smaller in absolute magnitude than the β shifts, contrary to some (2), but not all (4), theoretical predictions: secondly, the γ shifts for primary amines* are not normally opposite in sign to the β shifts; third, with 1-aminoadamantane and $Ni(AcAc)_2$, the α and β shifts have the same sign; finally, the ^{13}C shifts observed for alcohols are all of the same sign and downfield.

We have pointed out elsewhere (3) that the proton signals seem much less subject to contact contributions than carbon signals with lanthanide-shift reagents, and this effect is borne out here with $Ni(AcAc)_2$ and 1-butyl- and 2-butylamines. With $Ni(AcAc)_2$, the dipolar contributions are expected to be small because the g tensor should be more or less isotropic and the contact contributions should then be dominant. In accord with this expectation, the proton shifts (in ppm) are quite small compared to the carbon shifts (in ppm). With $Co(AcAc)_2$, the dipolar contributions should be significant, and now the proton shifts can be seen to be much larger and all positive†. Although the procedure hardly seems theoretically justifiable, we have found for several compounds that the differences between the nickel- and cobalt-induced shift changes for either the proton or carbon resonances give a rather reasonable facsimile of the pattern of shifts induced by lanthanide-shift reagents for the same compound‡.

If we take the $Ni(AcAc)_2$ results as being indicative primarily of the contact contributions to the carbon shifts, it is clear that the α-carbon resonance must be influenced by at least two mechanisms operating in opposite directions. One of these can be spin polarization, which has been shown to be important for lanthanide chelates and amines and alcohols (3, 5).‡ This effect is expected to be large and have opposite signs at the α and β carbons, and small at the α hydrogen, with the same sign as for the β carbon. Overlaying this effect must be an opposing contact effect that operates over all the carbons with the same sign, and falls off strongly with distance, but is felt appreciably out as far as the γ carbon. This opposing effect could be the σ-delocalization mechanism discussed by Fitzgerald and Drage (6). This effect clearly must have considerable structural specificity because it becomes much larger in amines as the α carbon becomes more substituted [the ratios of $Ni(AcAc)_2$-induced α/β ^{13}C shifts in 2-butylamine and 1-aminoadamantane are −0.4 and +0.1, respectively] and, furthermore, the γ shift of C6 (−35 ppm) in *exo*-norbornylamine is much larger than for C4 or C7 (about 0 ppm) (3).

* The situation appears to be different with secondary amines such as piperidine (2), although we find the α/γ carbon shift ratio for piperidine with $Ni(AcAc)_2$ to be +20/1 rather than the +10/1 reported. It seems possible that the magnitudes of the other small γ shifts (2) may be similarly uncertain for failure to use an internal reference or apply susceptibility corrections.

† The general pattern of results with respect to the dipolar shift with $Ni(AcAc)_2$ and $Co(AcAc)_2$ is in agreement with recent predictions; McGarvey, B. R. (1972) *J. Amer. Chem. Soc.* **94,** 1103–1108; Horrocks, W. D., Jr. Greenberg, E. S. (1971) *Inorg. Chem* **10,** 2190–2194; Horrocks, W. D., Jr. & Hall, D. D. (1971) *Inorg. Chem.* **10,** 2368–2370.

‡ Thus, a rather good fit between calculated and observed shifts for a purely dipolar mechanism with reasonable geometric parameters has been obtained by use of the algebraic difference between cobalt- and nickel-induced ^{13}C shifts observed for *exo*-norbornyl-amine by the procedure of Hawkes, G. E. Leibfritz, D., Roberts, D. W. & Roberts, J. D. (1973) *J. Amer. Chem. Soc.*, in press.

TABLE 1. *Proton and ^{13}C NMR shifts induced in primary amines and alcohols by nickel and cobalt acetylacetonates*

Compound	$(AcAc)_2$	Nucleus	Shifts, ppm* 1	2	3	4
1-Butylamine	Ni	^{13}C	229	—†	−62.9	∼0
		^{1}H	−14	−10	∼0	−2
	Co	^{13}C	390	−369	−21.7	20.9
		^{1}H	31.6	57.7	39.0	16.9
2-Butylamine	Ni	^{13}C	−208	140	−317	−35.9
		^{1}H	−9.0	—‡	−4.1, −23.9§	∼0
	Co	^{13}C	−129	292	−282	∼0
		^{1}H	62.4	17.1	70.7, 46.0§	33.1
1-Aminoadamantane	Ni	^{13}C	−21	−221	−47	5
	Co	^{13}C	72	−135	−17	+19
1-Butanol	Ni	^{13}C	−14.8	−42.9	−13.3	∼0
	Co	^{13}C	−18.8	−40.9	−9.5	∼0
1-Propanol	Ni	^{13}C	−16.4	−45.8	−16.7	—
	Co	^{13}C	−25.5	−56.2	−17.8	—

* Determined for 1 M solutions of substrate with three or four concentrations of metal acetylacetonate (usually 0.08 M maximum), and the slope was determined to give the effective shift for 1 M chelate concentration. The correlation coefficient for the linear least-squares fit of the shift to the concentration was usually 0.99+.

† Broadened too much for accurate measurement, but the shift was downfield.

‡ Too broadened to measure.

§ The β hydrogens, which are not magnetically equivalent by symmetry, are shifted very differently; this may be the result of differences in dipolar contributions, but might also reflect stereospecific contact effects (2).

It seems clear that the transition-metal chelates may have substantial utility as shift reagents in organic structural analysis by giving rather different information than can be obtained with the lanthanide chelates.

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